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Chiral imidazo[1,5-*a*]tetrahydroquinoline *N*-heterocyclic carbenes and their copper complexes for asymmetric catalysis

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ABSTRACT

Novel chiral imidazo[1,5-*a*]tetrahydroquinoline *N*-heterocyclic carbenes derived from β-pinene have been developed. The preliminary studies with both the in situ generated and preformed copper–carbene complexes have shown these chiral NHCs are efficient and selective ligands in the Cu-catalyzed asymmetric conjugate borylation of α,β-unsaturated esters.

1. Introduction

Since the isolation of stable imidazol-2-ylidene by Arduengo et al. in 1991,[1] *N*-heterocyclic carbenes (NHCs) have attracted much attention not only as versatile ligands in transition metal catalyzed reactions,[2] but also as useful nucleophilic organocatalysts.[3] Fine tuning of the electronic and steric properties has a dramatic impact on the reactivity and selectivity of NHCs. One of the main strategies to tune the electronic properties of NHCs is the construction of annulated bicyclic systems. For example, benzimidazole carbenes **1**[4] exhibit modified properties with respect to Arduengo's original imidazol-2-ylidenes **2**. Recently a pyrido-annulated bicyclic system, imidazo[1,5-*a*]pyridin-3-ylidenes **3**, has been developed independently by Lassaletta[5] and Glorius.[6] It was found that the pyrido-annulation significantly influences the σ-donor and π-acceptor properties of carbenes. An interesting electronic modulation was achieved by through-space communications between the carbene unit and the cyclophane arene in a planar chiral imidazo[1,5-*a*]pyridin-3-ylidenes.[7,8] On the other hand, fused cyclic structures are also of interest in tuning the steric properties of NHCs, as it has been shown computationally that the rotational lability of the carbene can greatly influence the behavior and dynamics of the NHC-bound metal complex.[9] The rigid C_2- and C_1-symmetric chiral NHCs **4**[10] and **5**[10a,11] that have annulated aliphatic rings such as an oxazolidine have shown a particular applicability as ligands in α-arylations[10e] and hydroarylations.[10f] In these NHCs, the internal rotation around the N–C (substituent) axis is blocked and the sterically demanding substituents close to carbene centers have the same orientation as the ligating atom, thus favoring high asymmetric induction. On this basis, we designed β-pinene derived chiral tetrahydroquinoline annulated imidazolylidenes **6** as the hybrid of NHCs **3** and **5**, in order to allow for modification of the electronic behavior as well as the control of the stereochemistry on the backbone of the NHC. Both the electronic and steric properties of NHCs are also expected to be finely tuned by different substitutions on the *N*-aryl group (Fig. 1). Herein we report the synthesis of these chiral imidazo[1,5-*a*]tetrahydroquinoline-3-ylidenes and their copper complexes as well as their application in asymmetric catalysis.

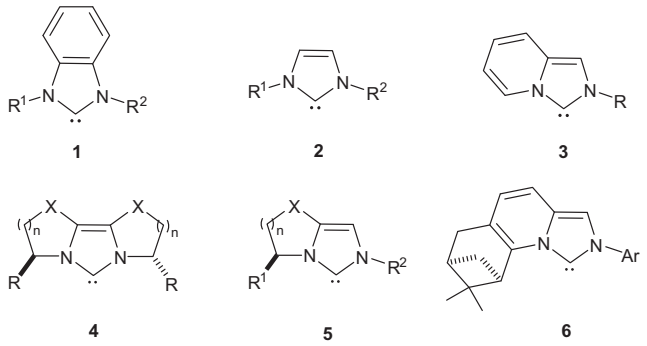

Figure 1. Typical examples of *N*-heterocyclic carbenes.

2. Results and discussion

The chiral imidazo[1,5-*a*]tetrahydroquinoline NHCs were synthesized from commercially available β-pinene. Following the procedure reported in the literature,[12] β-pinene was ozonolyzed to give nopinone **7** (92%), which was treated with methyl propiolate and ammonia in an autoclave at 140 °C to afford pyridone **8** in 63%. Treatment of pyridone **8** with triflic anhydride in the presence of triethylamine gave pyridyl triflate **9** in 92% yield.[12] The palla-

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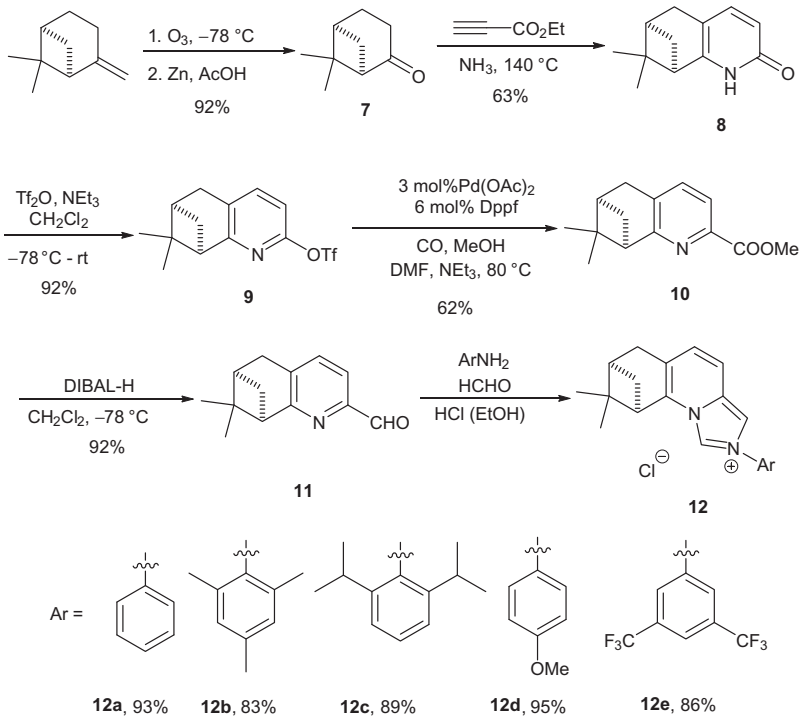
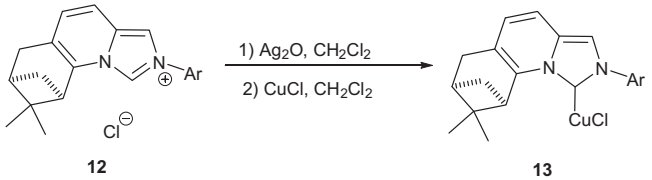


Scheme 1. Synthesis of β-pinene derived imidazo[1,5-*a*]tetrahydroquinolinium salts **12**.

dium-catalyzed carbonylation of triflate **9** in methanol afforded methyl ester **10** in 70%, which was reduced to aldehyde **11** by DIBAL-H at −78 °C.[12b] For the construction of the imidazo[1,5-*a*]tetrahydroquinolinium core, the one-step methodology recently reported by Aron was applied.[8b] In the presence of anhydrous HCl in ethanol, aldehyde **11** was condensed smoothly with formalin and aniline to give imidazo[1,5-*a*]tetrahydroquinolinium salt **12a** in 93% yield. Varying the substituents of anilines, other NHC precursors **12b–e** with different electronic and steric properties were synthesized (83–95%) (Scheme 1).

The reaction of chiral imidazo[1,5-*a*]tetrahydroquinolinium salts **12** with Ag_2O in CH_2Cl_2 at rt produced silver–carbene complexes, which were immediately transmetallated with CuCl in CH_2Cl_2 to afford chiral copper complexes **13** as white to pale yellow solids in high yields (Scheme 2).



13a: Ar = Ph, 85%
13b: Ar = 2,4,6-$Me_3C_6H_2$, 93%
13c: Ar = 2,6-$i Pr_2C_6H_3$, 95%
13d: Ar = 4-$MeOC_6H_4$, 91%
13e: Ar = 3,5-$(CF_3)_2C_6H_3$, 89%

Scheme 2. Synthesis of copper complexes **13**.

In order to test the applicability of our novel chiral NHC ligands in asymmetric catalysis, the asymmetric copper catalyzed β-borylation of α,β-unsaturated carbonyl compounds with bis(pinacolato)diboron (B_2pin_2) was envisioned as a suitable reaction, which provides boronic esters as useful synthetic intermediates that can be readily converted into amine, alcohol, alkyl, and aryl functionalities.[13] In 2009, Fernández et al. reported the first application of chiral NHC ligands in the asymmetric Cu-catalyzed borylation of α,β-unsaturated esters.[14] It was found that C_1-symmetric NHCs, such as **14**, generally outperformed their C_2-symmetric analogues in terms of asymmetric induction. Later on, Hoveyda reported the enantioselective synthesis of boron-substituted quarternary carbons by NHC-Cu catalyzed boronate conjugated addition to β,β-disubstituted substrates.[15] In agreement with the observation made by Fernández, a readily accessible C_1-symmetric NHC **15** gave excellent results. The potential of C_1-symmetric NHC ligands in the copper catalyzed 1,4-addition of boron nucleophiles was further showcased by Hong[11] in the conjugate borylation of α,β-unsaturated amides using NHC **16**. A C_1-symmetric chiral 6-membered NHC **17** was recently developed by McQuade,[16] the copper complex of which showed good enantioselectivity and high activity in the symmetric β-borylation of α,β-unsaturated esters. On the basis of the reported success of C_1-symmetric chiral NHC ligands in copper catalyzed β-borylations, we chose the conjugate borylation of ethyl cinnamate as a model to determine the asym-

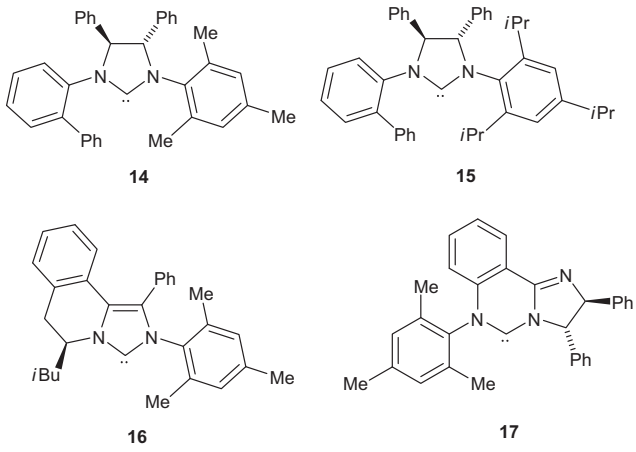
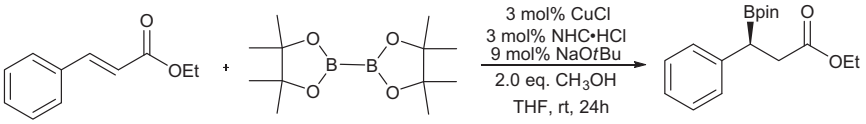


Figure 2. C_1-Symmetric chiral NHC ligands in copper catalyzed conjugate borylation.

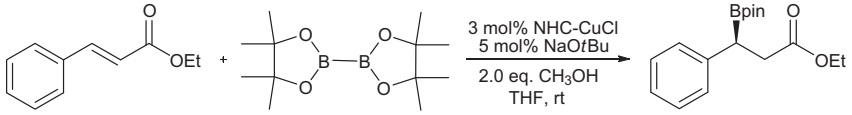
Table 1
CuCl/NHC mediated asymmetric β-borylation of ethyl cinnamate[a]



Entry	NHC·HCl	Conv.[b] (%)	Yield[c] (%)	ee[d] (%)
1	**12a**	93	90	14 (*S*)
2	None	0	0	/
3	**12b**	86	81	50 (*S*)
4	**12c**	71	58	65 (*S*)
5	**12d**	91	83	18 (*S*)
6	**12e**	94	89	16 (*S*)

[a] Reaction conditions: 1.0 equiv of ethyl cinnamate (0.15 M), 1.1 equiv of bis(pinacolato)diboron.
[b] Determined by ^{1}H NMR.
[c] Isolated yield.
[d] Determined by HPLC after conversion to an alcohol by treatment with $NaBO_3$.

Table 2
NHC–CuCl mediated asymmetric β-borylation of ethyl cinnamate[a]



Entry	NHC–CuCl	Time (h)	Conv.[b] (%)	Yield[c] (%)	ee[d] (%)
1	**13a**	12	92	87	28 (*S*)
2	**13b**	12	91	84	56 (*S*)
3	**13c**	24	78	72	62 (*S*)
4	**13d**	6	99	94	29 (*S*)
5	**13e**	8	99	91	21 (*S*)

[a] Reaction conditions: 1.0 equiv of ethyl cinnamate (0.15 M), 1.1 equiv of bis(pinacolato)diboron.
[b] Determined by ^{1}H NMR.
[c] Isolated yield.
[d] Determined by HPLC after conversion to an alcohol by treatment with $NaBO_3$.

metric inducing ability of our chiral imidazo[1,5-*a*]tetrahydroquinoline NHCs **6**. To date, no chiral imidazo[1,5-*a*]pyridin-3-ylidene has ever been used as a ligand in this reaction (Fig. 2).[17]

Imidazo[1,5-*a*]tetrahydroquinolinium salts **12** were first evaluated as the precursors of NHC ligands in the conjugate borylation of ethyl cinnamate (Table 1). In the presence of B_2pin_2 (1.1 equiv) and CH_3OH (2.0 equiv), the copper catalyst generated in situ from CuCl (3 mol %), imidazoliums **12a** (3 mol %), and NaO*t*Bu (9 mol %) was efficient to yield the β-borylation product in high yield in THF at room temperature (Table 1, entry 1). Controlled experiments indicated that the conjugate borylation did not take place in the absence of imidazo[1,5-*a*]tetrahydroquinolinium salt **12a** (Table 1, entry 2). A systematic investigation on the substituent effects of the imidazo[1,5-*a*]tetrahydroquinolinium salts **12** indicated that introduction of alkyl groups to the *ortho*-position of the *N*-phenyl ring of the NHC ligands notably increased the stereoselectivities but decreased the activities (Table 1, entries 3 and 4). The NHC ligand derived from imidazo[1,5-*a*]tetrahydroquinolinium salt **12c** was found to be the most selective one (Table 1, entry 4), which showed comparable enantioselectivity (65% ee) as C_1-symmetric NHC ligands **14** (61% ee) and **16** (53% ee). The introduction of electron donating or withdrawing groups to the *para*- or *meta*-position of the *N*-phenyl ring of the NHC ligands did not have much influence on either the catalytic activities or stereoselectivities (Table 1, entries 5 and 6).

The preformed copper complexes **13** were then screened as catalysts in the β-borylation of ethyl cinnamate. As can be seen from Table 2, the preformed NHC–CuCl complexes showed better catalytic activities than the in situ generated copper catalyst (vide supra), especially for those bearing electron donating or withdrawing groups to the *para*- or *meta*-position of the *N*-phenyl ring of the NHC ligands (Table 2, entries 4 and 5). The enantioselectivities were also improved by using the preformed NHC–CuCl complexes, except for **13c** which showed a lower enantioselectivity (63% ee, Table 2, entry 3) than the in situ generated copper catalyst from the corresponding NHC precursor **12c** (65% ee, Table 1, entry 4). Consistent with the observations of the in situ generated catalysts, higher stereoselectivities were induced by the sterically hindered complexes **13b** and **13c** (Table 2, entries 2 and 3).

3. Conclusion

In conclusion, we have designed and synthesized a new type of chiral imidazo[1,5-*a*]tetrahydroquinoline *N*-heterocyclic carbene precursors from β-pinene and prepared the copper complexes of these NHC ligands. The preliminary studies with the imidazo[1,5-*a*]tetrahydroquinolinium salts **12** and NHC–CuCl complexes **13** indicated that these novel NHCs were efficient and selective chiral ligands in the Cu-catalyzed asymmetric conjugate borylation of α,β-unsaturated esters. The sense of selectivity was strongly dependent on the steric properties of the *N*-heterocyclic moiety. An in-depth exploration of their use in asymmetric catalysis is currently in progress in our laboratories.

4. Experimental

4.1. General

Melting points were determined on a Yanaco MP-500 micro melting point apparatus and are uncorrected. Infrared spectra were measured with a Nicolet Avatar 330 FT-IR spectrometer using film

KBr pellet techniques. Optical rotations were measured with a Perkin–Elmer 341 automatic polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts are expressed in parts per million (δ) relative to an internal standard of residual chloroform (7.26 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR) or DMSO (2.50 ppm for ^{1}H NMR and 39.5 ppm for ^{13}C NMR). Mass spectra were recorded on a Bruker Dalton Esquire 3000 plus LC–MS apparatus. HRMS spectra were recorded on a 7.0T FT-MS. Silica gel (300–400 mesh) was used for flash column chromatograph, eluting (unless otherwise stated) with an ethyl acetate/petroleum ether (PE) (60–90 °C) or ethyl acetate/*n*-hexane mixture. THF was distilled over sodium benzophenone ketyl under N_2. Dichloromethane was distilled over calcium hydride under N_2.

4.2. Synthesis of (1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-one 7[12]

A solution of (−)-β-pinene (5.0 g, 36.7 mmol) in a mixture of MeOH (10 mL) and CH_2Cl_2 (10 mL) was cooled to −78 °C in a three-neck, round-bottomed flask. Ozone was bubbled through the solution by means of a sinter-glass-ended tube for 1.5 h until a blue color persisted. Nitrogen was then bubbled through the reaction mixture for 30 min, which was then allowed to warm to 0 °C. Acetic acid (10 mL) and zinc powder (7.2 g, 110 mmol) were then added portionwise. The resulting suspension was filtered, and the solid material was washed with CH_2Cl_2 repeatedly. The organic layer was carefully washed with a saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with CH_2Cl_2 (30 mL × 3), the combined organic layers were washed with water (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was further purified by vacuum distillation to afford **7** (4.67 g, 92%) as a colorless liquid. $[\alpha]_D^{20} = +29.8$ (*c* 2.5, $CHCl_3$); IR (film): 2952, 1713, 1457, 1367, 1197, 1027 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (s, 3H), 1.31 (s, 3H), 1.56 (d, *J* = 10.2 Hz, 1H), 1.89–1.96 (m, 1H), 1.99–2.07 (m, 1H), 2.19–2.24 (m, 1H), 2.32 (ddd, *J* = 19.1, 9.1, 2.1 Hz, 1H), 2.49–2.61 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 22.1, 25.3, 25.9, 32.8, 40.4, 41.2, 58.0, 215.1; ESI-MS (*m*/*z*): 161 [M+Na$^+$].

4.3. Synthesis of (6*R*,8*R*)-7,7-dimethyl-5,6,7,8-tetrahydro-6,8-methanoquinolin-2(1*H*)-one 8[12]

A solution of nopinone (3.0 g, 21.7 mmol) and ethylpropiolate (4.2 mL, 42 mmol) in a 7 M solution of ammonia in methanol (100 mL) was heated and stirred in an autoclave at 140 °C and 12 bar pressure for 15 h under a nitrogen atmosphere. The autoclave was cooled to ambient temperature and the reaction mixture was diluted with CH_2Cl_2, passed through a pad of silica gel, concentrated, and purified by flash column chromatography on silica gel (eluting with 1% CH_3OH/CH_2Cl_2) to give pure pyridone **8** (2.6 g, 63%) as a yellow amorphous solid. Mp 180–181 °C; $[\alpha]_D^{20} = +71.5$ (*c* 0.9, CH_2Cl_2); IR (film): 2888, 2880, 2790, 2785, 1670, 1655, 1600, 1575, 1500, 1448, 1425, 1375, 1368, 1325, 981, 895, 725, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.72 (s, 3H), 1.29 (d, *J* = 9.6 Hz, 1H), 1.36 (s, 3H), 2.22–2.26 (m, 1H), 2.59–2.67 (m, 3H), 2.83 (t, *J* = 5.4 Hz, 1H), 6.35 (d, *J* = 9.0 Hz, 1H), 7.25 (d, *J* = 9.0 Hz, 1H) 13.77 (b, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 25.7, 29.4, 30.7, 39.5, 40.5, 45.0, 111.0, 115.2, 142.6, 153.8, 164.5; ESI-MS (*m*/*z*): 212 [M+Na$^+$].

4.4. Synthesis of (6*R*,8*R*)-7,7-dimethyl-5,6,7,8-tetrahydro-6,8-methanoquinolin-2-yl trifluoromethanesulfonate 9[12]

To a solution of pyridone **8** (480 mg, 2.54 mmol) and anhydrous triethylamine (0.53 mL, 3.81 mmol) in CH_2Cl_2 (10 mL) was added trifluoromethanesulfonic anhydride (0.51, 3.05 mmol) with stirring under a nitrogen atmosphere at −78 °C. The reaction mixture was then stirred at the same temperature over a period of 1.5 h. Next, it was quenched by pouring onto ice. The organic layer was washed with 10% aqueous NaOH (10 mL), extracted with CH_2Cl_2 (10 mL × 3), dried over Na_2SO_4, concentrated and purified via flash chromatography on silica gel (eluting with 5% ethyl ether/petroleum ether) to afford pyridyl triflate **9** (750 mg, 92%) as a colorless liquid. $[\alpha]_D^{20} = -8.9$ (*c* 1.0 , CH_2Cl_2); IR (film): 2980, 2965, 1640, 1610, 1558, 1525, 1444, 1375, 1112, 998, 875, 792, 680 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (s, 3H), 1.28 (d, *J* = 9.9 Hz, 1H), 1.42 (s, 3H), 2.33–2.37 (m, 1H), 2.70–2.75 (m, 1H), 2.93–2.96 (m, 3H), 6.94 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 25.8, 30.5, 30.8, 39.1, 39.9, 49.7, 111.9, 118.7 (q, $^1J_{CF}$ = 318 Hz), 131.2, 139.3, 152.9, 166.7; ESI-MS (*m*/*z*): 344 [M+Na$^+$].

4.5. Synthesis of (6*R*,8*R*)-methyl 7,7-dimethyl-5,6,7,8-tetrahydro-6,8-methanoquinoline-2-carboxylate 10[12b]

A Schlenk flask was charged with pyridyl triflate **9** (207 mg, 0.64 mmol), palladium acetate (4.3 mg, 0.019 mmol), and Dppf (21.4 mg, 0.038 mmol) and placed under nitrogen via three vacuum/nitrogen cycles. Next, it was connected to a balloon flushed with carbon monoxide. The degassed triethylamine (0.19 mL, 1.32 mmol), dimethyl formamide (2.48 mL), and methanol (1.34 mL) were added to the flask via syringe. The mixture was then heated at 80 °C for 24 h. Next, it was cooled to the room temperature, concentrated and purified by flash chromatography on silica gel (eluting with 10% ethyl acetate/petroleum ether) to obtain the methyl ester **10** (92 mg, 62%) as an oil. $[\alpha]_D^{20} = -9.8$ (*c* 1.5, CH_2Cl_2); IR (film): 2990, 2948, 2840, 1735, 1568, 1475, 1440, 1380, 1375, 1156, 1110, 891, 760, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.63 (s, 3H), 1.25 (d, *J* = 10.0 Hz, 1H), 1.39 (s, 3H), 2.30–2.34 (m, 1H), 2.69–2.74 (m, 1H), 2.98–2.99 (m, 2H), 3.16 (t, 5.6 Hz, 1H), 3.95 (s, 3H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 25.8, 30.6, 31.6, 39.0, 39.8, 50.3, 52.7, 123.3, 135.1, 135.7, 143.7, 166.2, 166.8; ESI-MS (*m*/*z*): 254 [M+Na$^+$].

4.6. Synthesis of (6*R*,8*R*)-7,7-dimethyl-5,6,7,8-tetrahydro-6,8-methanoquinoline-2-carbaldehyde 11[12b]

To a solution of ester **10** in CH_2Cl_2 (60 mg, 0.26 mmol) at −78 °C was added a solution of DIBAL-H (1.0 M in hexane, 0.52 mL, 0.52 mmol) dropwise. After stirring for 1 h at the same temperature, the reaction was quenched by the dropwise addition of methanol (0.5 mL). After stirring for 15 min, a saturated aqueous solution of Rochelle's salt (0.5 mL) was added at −78 °C. Next, the mixture was warmed up to room temperature and stirred overnight. The reaction mixture was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica gel (eluting with 5% ethyl acetate/petroleum ethyl) to give aldehyde **11** (48 mg, 92%) as an oil, which solidified upon refrigeration. Mp 46–47 °C; $[\alpha]_D^{20} = -27.8$ (*c* 1.0, CH_2Cl_2); IR (film): 2880, 2775, 1725, 1625, 1598, 1575, 1425, 1411, 1400, 1325, 981, 875, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.64 (s, 3H), 1.28 (d, *J* = 9.9 Hz, 1H), 1.43 (s, 3H), 2.33–2.37 (m, 1H), 2.73–2.79 (m, 1H), 3.00–3.01 (m, 2H), 3.09 (t, *J* = 5.6 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 9.99 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 25.8, 30.6, 31.7, 39.1, 39.8, 50.2, 120.3, 135.7, 136.2, 149.1, 167.1, 193.3; ESI-MS (*m*/*z*): 202 [M+H$^+$].

4.7. General procedure for the synthesis of imidazo[1,5-*a*]tetrahydroquinolinium salts 12

According to the modified procedure reported by Aron et al.,[8b] to a solution of aldehyde **11** (1.0 equiv) in EtOH (0.5 M) were added aniline (1.0 equiv), formalin (1.5 equiv), and 3 M HCl in EtOH (1.5 equiv). The reaction mixture was stirred at room temperature until aldehyde **11** was consumed as determined by TLC. Next, the reaction mixture was concentrated and purified by flash chromatography on silica gel (eluting with 10% CH_3OH/CH_2Cl_2) to afford the imidazo[1,5-*a*]tetrahydroquinolinium salts **12**.

4.7.1. Synthesis of (7*R*,9*R*)-8,8-dimethyl-2-phenyl-6,7,8,9-tetrahydro-7,9-methanoimidazo[1,5-*a*]quinolin-2-ium chloride 12a

Treatment of aldehyde **11** (70 mg, 0.35 mmol) in EtOH (0.7 mL) with aniline (0.032 mL, 0.35 mmol), formalin (0.042 mL, 0.52 mmol), and 3 M HCl in EtOH (0.17 mL) at room temperature for 3 h afforded imidazo[1,5-*a*]tetrahydroquinolinium salt **12a** (105 mg, 93%) as colorless crystals. Mp 121–122 °C; $[\alpha]_D^{20} = +60.6$ (*c* 1.1, CH_3OH); IR (KBr): 2956, 2940, 2909, 2888, 1652, 1259, 1030, 814, 755, 681 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 0.73 (s, 3H), 1.38 (d, J = 9.4 Hz, 1H), 1.50 (s, 3H), 2.38–2.40 (m, 1H), 2.81–2.86 (m, 1H), 2.90–3.06 (m, 2H), 3.74 (t, J = 5.3 Hz, 1H), 7.28 (d, J = 9.3 Hz, 1H), 7.63–7.74 (m, 3H), 7.78 (d, J = 9.3 Hz, 1H), 8.00 (d, J = 7.8 Hz, 2H), 8.79 (s, 1H), 10.49 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.4, 25.9, 30.7, 31.5, 39.5, 40.1 41.8, 112.4, 115.5, 122.5, 123.2, 127.7, 130.2, 130.7, 130.8, 135.7, 139.7; HRMS (ESI) calcd for $[C_{20}H_{21}N_2]^+$ $(M-Cl)^+$: 289.1705; found: 289.1706.

4.7.2. Synthesis of (7*R*,9*R*)-2-mesityl-8,8-dimethyl-6,7,8,9-tetrahydro-7,9-methanoimidazo[1,5-*a*]quinolin-2-ium chloride 12b

Treatment of aldehyde **11** (100 mg, 0.50 mmol) in EtOH (1.0 mL) with 2,4,6-trimethylaniline (0.070 mL, 0.50 mmol), formalin (0.061 mL, 0.75 mmol), and 3 M HCl in EtOH (0.25 mL) at room temperature for 12 h afforded the product imidazo[1,5-*a*]tetrahydroquinolinium salt **12b** (152.3 mg, 83%) as colorless crystals. Mp 262–263 °C; $[\alpha]_D^{20} = +38.4$ (*c* 1.3, $CHCl_3$); IR (film): 2934, 1553, 1386, 1284, 1185, 1138, 755, 681 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.73 (s, 3H), 1.42 (d, J = 9.6 Hz, 1H), 1.50 (s, 3H), 2.02 (s, 3H), 2.05 (s, 3H), 2,37–2.39 (m, 4H), 2,79–2.84 (m, 1H), 2.92–3.03 (m, 2H), 3.67 (t, J = 5.2 Hz, 1H), 7.19 (s, 2H), 7.31 (d, J = 9.6 Hz, 1H), 7.82 (d, J = 9.6 Hz, 1H), 8.44 (s, 1H), 10.33 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 17.4, 17.5, 21.1, 21.2, 25.8, 30.7, 31.6, 39.5, 40.1, 42.0, 115.1, 115.7, 122.4, 125.2, 127.6, 129.6, 129.7, 130.1, 132.2, 134.6, 134.7, 139.9, 140.9; HRMS (ESI) calcd for $[C_{23}H_{27}N_2]^+$ $(M-Cl)^+$: 331.2174; found: 331.2172.

4.7.3. Synthesis of (7*R*,9*R*)-2-(2,6-diisopropylphenyl)-8,8-dimethyl-6,7,8,9-tetrahydro-7,9-methanoimidazo[1,5-a] quinolin-2-ium chloride 12c

Treatment of aldehyde **11** (100 mg, 0.50 mmol) in EtOH (1.0 mL) with 2,6-diisopropylaniline (0.11 mL, 0.50 mmol), formalin (0.061 mL, 0.75 mmol), and 3 M HCl in EtOH (0.25 mL) at room temperature for 12 h afforded the product imidazo[1,5-*a*]tetrahydroquinolinium salt **12c** (182 mg, 89%) as colorless crystals. Mp 289–290 °C; $[\alpha]_D^{20} = +26.0$ (*c* 1.0, $CHCl_3$); IR (film): 3431, 3067, 2971, 2931, 1550, 1516, 1259, 1188, 1021, 814 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.79 (s, 3H), 1.13 (d, J = 6.8 Hz, 3H), 1.15 (d, J = 6.8 Hz, 3H), 1.25 (d, J = 6.8 Hz, 3H), 1.28 (d, J = 6.8 Hz, 3H), 1.48 (d, J = 9.7 Hz, 1H), 1.57 (s, 3H), 2.05–2.12 (m, 1H), 2.18–2.24 (m, 1H), 2.41–2.44 (m, 1H), 2.91–3.08 (m, 3H), 4.43 (t, J = 5.4 Hz, 1H), 7.21 (d, J = 9.3 Hz, 1H), 7.31–7.33 (m, 2H), 7.54 (t, J = 7.8 Hz, 1H), 7.71 (s, 1H), 7.75 (d, J = 9.3 Hz, 1H), 11.3 (s 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 24.3, 24.4, 24.7, 25.4, 28.6, 28.7, 31.0, 31.9, 39.7, 40.1, 42.5, 114.6, 114.8, 122.9, 124.4, 124.5, 126.7, 128.0, 130.0, 131.0, 131.7, 141.5, 145.0, 145.1; HRMS (ESI) calcd for $[C_{26}H_{33}N_2]^+$ $(M-Cl)^+$: 373.2644; found: 373.2650.

4.7.4. Synthesis of (7*R*,9*R*)-2-(4-methoxyphenyl)-8,8-dimethyl-6,7,8,9-tetrahydro-7,9-methanoimidazo[1,5-a]quinolin-2-ium chloride 12d

Treatment of aldehyde **11** (113 mg, 0.56 mmol) in EtOH (1.1 mL) with *p*-anisidine (69.1 mg, 0.56 mmol), formalin (0.068 mL, 0.84 mmol), and 3 M HCl in EtOH (0.28 mL) at room temperature for 1 h afforded imidazo[1,5-*a*]tetrahydroquinolinium salt **12d** (188.8 mg, 95%) as a yellow solid. Mp 142–143 °C; $[\alpha]_D^{20} = +68.8$ (*c* 0.8, $CHCl_3$); IR (film): 2968, 2918, 1648, 1546, 1370, 1265, 1244, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.73 (s, 3H), 1.37 (d, J = 9.7 Hz, 1H), 1.55 (s, 3H), 2.35–2.39 (m, 1H), 2.86–2.99 (m, 3H), 3.76 (s, 3H), 4.45 (t, J = 5.4 Hz, 1H), 6.98 (d, J = 9.1 Hz, 2H), 7.04 (d, J = 9.3 Hz, 1H), 7.55 (d, J = 9.3 Hz, 1H), 8.08 (d, J = 9.1 Hz, 2H), 8.20 (s, 1H), 11.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 25.5, 30.9, 31.8, 39.8, 40.2, 42.3, 55.7, 110.2, 114.4, 115.3 (2C), 122.4, 123.4, 123.9 (2C), 127.4, 127.9, 130.2 141.4, 160.7; HRMS (ESI) calcd for $[C_{21}H_{23}N_2O]^+$ $(M-Cl)^+$: 319.1810; found: 319.1809.

4.7.5. Synthesis of (7*R*,9*R*)-2-(3,5-bis(trifluoromethyl)phenyl)-8,8-dimethyl-6,7,8,9-tetrahydro-7,9-methanoimidazo[1,5-*a*] quinolin-2-ium chloride 12e

Treatment of aldehyde **11** (113 mg, 0.56 mmol) in EtOH (1.1 mL) with 3,5-bis(trifluoromethyl)aniline (0.090 mL, 0.56 mmol), formalin (0.068 mL, 0.84 mmol), and 3 M HCl in EtOH (0.18 mL) at room temperature for 12 h afforded imidazo[1,5-*a*]tetrahydroquinolinium salt **12e** (221.9 mg, 86%) as a yellow solid. Mp 129–130 °C; $[\alpha]_D^{20} = +34.4$ (*c* 1.0, $CHCl_3$); IR (film): 2965, 2925, 2869, 1652, 1546, 1463, 1367, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.74 (s, 3H), 1.38 (d, J = 9.7 Hz, 1H), 1.50 (s, 3H), 2.38–2.40 (m, 1H), 2.84–3.03 (m, 3H), 4.38 (t, J = 5.4 Hz, 1H), 7.12 (d, J = 9.4 Hz, 1H), 7.84 (d, J = 9.4 Hz, 1H), 7.91 (s, 1H), 8.94 (s, 2H), 9.16 (s, 1H), 12.2 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 25.4, 30.8, 31.8, 39.8, 40.1, 42.3, 112.0, 115.5, 121.0, 123.6, 123.7, 123.9, 124.2, 127.9, 130.9, 133.7 (q, $^1J_{CF}$ = 34.0 Hz), 136.5, 141.1; HRMS (ESI) calcd for $[C_{22}H_{19}F_6N_2]^+$ $(M-Cl)^+$: 425.1452; found: 425.1449.

4.8. General procedure for the synthesis of NHC–CuCl complex 13

A solution of imidazo[1,5-*a*]tetrahydroquinolinium salt **12** (1.0 equiv) and Ag_2O (0.6 equiv) in CH_2Cl_2 (0.2 M) was stirred for 12 h at room temperature under N_2 and then filtered through a pad of Celite. The filtrate was concentrated under reduced pressure to afford the crude silver–carbene complex, which was used immediately in the next step without further purification.

A solution of the crude silver–carbene complex and CuCl (1.0 equiv) in CH_2Cl_2 (0.2 M) was stirred for 4 h at room temperature under N_2 and then filtered through a pad of Celite. The filtrate was concentrated under reduced pressure to give the copper complex **13**.

4.8.1. Synthesis of ((7*R*,9*R*)-8,8-dimethyl-2-phenyl-1,2,6,7,8,9-hexahydro-7,9-methanoimidazo[1,5-a]quinolin-1-yl)copper(I) chloride 13a

^1H NMR (400 MHz, $CDCl_3$) δ 0.81 (s, 3H), 1.40 (d, J = 9.5 Hz, 1H), 1.55 (s, 3H), 2.37–2.40 (m, 1H), 2.81–2.95 (m, 3H), 5.08 (t, J = 5.6 Hz, 1H), 6.82 (d, J = 9.2 Hz, 1H), 7.27 (d, J = 9.2 Hz, 1H), 7.45–7.54 (m, 4H), 7.72 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 25.8, 31.1, 32.0, 39.9, 40.2, 43.9, 111.1, 114.1, 118.3, 124.6 (2C), 125.6, 129.2, 129.8 (2C), 131.8, 140.8, 143.3.

HRMS (ESI) calcd for $[C_{20}H_{20}ClCuN_2Na]^+$ (M+Na$^+$): 409.0509; found: 409.0508.

4.8.2. Synthesis of ((7*R*,9*R*)-2-mesityl-8,8-dimethyl-1,2,6,7,8,9-hexahydro-7,9-methanoimidazo[1,5-*a*]quinolin-1-yl)copper(I) chloride 13b

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (s, 3H), 1.44 (d, J = 9.6 Hz, 1H), 1.54 (s, 3H), 1.97 (s, 3H), 1.98 (s, 3H), 2.34 (s, 3H), 2.36–2.41 (m, 1H), 2.81–2.96 (m, 3H), 4.98 (t, J = 5.6 Hz, 1H), 6.83 (d, J = 9.2 Hz, 1H), 6.98 (s, 2H), 7.18 (s, 1H), 7.27 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 21.0, 21.1, 25.8, 29.7, 31.1, 31.9, 39.9, 40.2, 44.0, 111.8, 114.2, 118.0, 125.3, 129.3 (2C), 131.2, 134.2, 134.3, 136.4, 139.4, 143.4. HRMS (ESI) calcd for $[C_{23}H_{26}ClCuN_2Na]^+$ (M+Na$^+$): 451.0978; found: 451.0972.

4.8.3. Synthesis of ((7*R*,9*R*)-2-(2,6-diisopropylphenyl)-8,8-dimethyl-1,2,6,7,8,9-hexahydro-7,9-methanoimidazo[1,5-*a*]quinolin-1-yl)copper(I) chloride 13c

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (s, 3H), 1.09–1.12 (m, 6H), 1.23–1.26 (m, 6H), 1.47 (d, J = 9.5 Hz, 1H), 1.55 (s, 3H), 2.13–2.26 (m, 2H), 2.38–2.42 (m, 1H), 2.83–2.98 (m, 3H), 5.00 (t, J = 5.5 Hz, 1H), 6.86 (d, J = 9.2 Hz, 1H), 7.22 (s, 1H), 7.26–7.30 (m, 3H), 7.48 (t, J = 7.8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 24.5, 24.6 (2C), 25.7, 28.2, 28.3, 29.7, 31.2, 32.0, 39.9, 40.2, 44.0, 113.1, 114.1, 118.2, 124.0 (2C), 125.5, 130.5, 130.9, 135.7, 143.5, 145.3, 145.4. HRMS (ESI) calcd for $[C_{26}H_{32}ClCuN_2Na]^+$ (M+Na$^+$): 493.1448; found: 493.1450.

4.8.4. Synthesis of ((7*R*,9*R*)-2-(4-methoxyphenyl)-8,8-dimethyl-1,2,6,7,8,9-hexahydro-7,9-methanoimidazo[1,5-*a*]quinolin-1-yl)copper(I) chloride 13d

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (s, 3H), 1.39 (d, J = 9.4 Hz, 1H), 1.55 (s, 3H), 2.36–2.40 (m, 1H), 2.81–2.93 (m, 3H), 3.85 (s, 3H), 5.05 (t, J = 5.5 Hz, 1H), 6.80 (d, J = 9.2 Hz, 1H), 7.01 (d, J = 8.9 Hz, 2H), 7.25 (d, J = 9.2 Hz, 1H), 7.48 (s, 1H), 7.61 (d, J = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 25.8, 31.1, 31.9, 39.9, 40.2, 43.9, 55.6, 111.3, 114.1, 114.9 (2C), 118.2, 125.4, 125.7 (2C), 131.6, 133.9, 143.3, 160.1. HRMS (ESI) calcd for $[C_{21}H_{22}ClCuN_2ONa]^+$ (M+Na$^+$): 439.0614; found: 439.0609.

4.8.5. Synthesis of ((7*R*,9*R*)-2-(3,5-bis(trifluoromethyl)phenyl)-8,8-dimethyl-1,2,6,7,8,9-hexahydro-7,9-methanoimidazo[1,5-*a*]quinolin-1-yl)copper(I) chloride 13e

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (s, 3H), 1.41 (d, J = 9.5 Hz, 1H), 1.57 (s, 3H), 2.40–2.43 (m, 1H), 2.84–2.98 (m, 3H), 5.03 (t, J = 5.4 Hz, 1H), 6.91 (d, J = 9.3 Hz, 1H), 7.32 (d, J = 9.3 Hz, 1H), 7.63 (s, 1H), 8.03 (s, 1H), 8.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 25.7, 31.1, 32.0, 40.0, 40.2, 44.2, 110.6, 114.1, 119.3, 121.1, 123.1, 123.9, 125.3, 126.6, 132.5, 133.3, 133.6, 142.0, 143.4. HRMS (ESI) calcd for $[C_{22}H_{18}ClCuF_6N_2Na]^+$ (M+Na$^+$): 545.0256; found: 545.0258.

4.9. General procedure for the asymmetric β-borylation using in situ generated copper catalysts

To a flame-dried Schlenk flask was added CuCl (3 mol %), NHCs·HCl **12** (3 mol %), NaO*t*Bu (9 mol %), and THF (0.15 M). The reaction mixture was stirred for 30 min at room temperature under N_2. Next, bis(pinacolato)diboron (1.1 equiv) dissolved in THF was added followed by ethyl cinnamate (1.0 equiv) and methanol (2.0 equiv). The reaction mixture was then sealed and stirred at room temperature for 24 h. The reaction mixture was filtered through a pad of Celite, concentrated and purified by column chromatography (Hexane:EtOAc = 20:1) to afford the desired product.

4.10. General procedure for the asymmetric β-borylation using preformed copper complexes 13

To a flame-dried Schlenk flask were added NHC–CuCl **13** (3 mol %), NaO*t*Bu (5 mol %), bis(pinacolato)diboron (1.1 equiv), and THF (0.15 M). The reaction mixture was stirred for 10 min at room temperature under N_2. Next, ethyl cinnamate (1.0 equiv) and methanol (2.0 equiv) were added successively. The reaction mixture was then sealed and stirred at room temperature for 6–24 h. The reaction mixture was filtered through a pad of Celite, concentrated and purified by column chromatography (Hexane:EtOAc = 20:1) to afford the desired product.

4.11. Ethyl 3-pheny-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate[18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20–1.26 (m, 15H), 2.67 (dd, J = 6.0, 16.0 Hz, 1H), 2,74–2,78 (m, 1H), 2,90 (dd, J = 9.9, 16.0 Hz, 1H), 4.08–4.17 (m, 2H), 7.15–7.30 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 24.5, 24.6, 37.3, 60.4, 83.5, 125.7, 128.2, 128.5, 141.4, 173.4.

4.12. Ethyl 3-hydroxy-3-phenylpropanoate[18]

For the determination of the enantioselectivity, the resulting boronate (1.0 equiv) and $NaBO_3{\cdot}4H_2O$ (5.0 equiv) were dissolved in THF (0.2 M) and H_2O (0.2 M). The reaction mixture was stirred at room temperature for 4 h. After complete consumption of the boronate, the mixture was extracted with EtOAc, concentrated and purified by column chromatography (Hexane:EtOAc = 10:1) to afford the alcohol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, J = 7.2 Hz, 3H), 2.68–2.81 (m, 2H), 3.45 (d, J = 3.2 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 5.12–5.16 (m, 1H), 7.28–7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 43.4, 60.9, 70.3, 125.7, 127.8, 128.5, 142.6, 172.4. The ee was measured by chiral HPLC using an OD-H column (*i*-PrOH–hexane, 10:90, 1.0 mL/min, 250 nm): t_R = 8.2 min (*S*), 10.5 min (*R*).

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